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Aryl Trialkylsilyl Ketenes: Acid-Catalyzed Synthesis from 1-Aryl-2-diazo-2-trialkylsilylethanones and Their Conversion into 3-Silyl-1-silyloxyallenes

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Aryl-substituted α-silyl α-diazo ketones are readily transformed into aryl silyl ketenes in the presence of a catalytic amount of triflic acid. Thus, a convenient method to prepare these silyl ketenes becomes available, which combines two steps, silylation of an aryl diazomethyl ketone and acid-induced Wolff rearrangement of the formed α-silyl α-diazo ketone, in a one-pot procedure. It appears that the trialkylammonium salt, which is formed in the silylation step, can also catalyze the Wolff rearrangement, but distinctly more slowly than the proton acid. The silyl ketenes react smoothly with α-silyl α-diazo ketones to form 3-silyl-1-silyloxyallenes in fairly good yields.

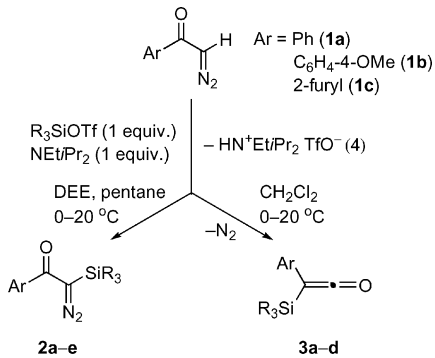
Introduction

Due to their remarkable chemical stability, silyl ketenes have received much attention as versatile building blocks in organic synthesis.[1,2] For example, trialkylsilyl ketenes can be transformed into allenylsilanes with phosphonium ylides by Wittig olefination[3,4] and also with organometallic methylenation reagents.[4] The long-known[5] reactivity of ketenes towards diazoalkanes has also been extended to silyl ketenes.[1,2] Of particular interest to the present study are reactions between (diazomethyl)trialkylsilanes and trimethylsilyl ketene, which afford 1-trimethylsilyl-2-trialkylsilylcyclopropanones.[6] In contrast, when TMS-diazomethane is combined with phenyl (phosphoryl, sulfonyl, or vinyl) ketenes, the cyclopropanone adduct appears to be a reactive intermediate that readily decarbonylates to form β-(trimethylsilyl)styrenes [or 1-(trimethylsilyl)-1,3-dienes, in the case of a vinyl substituent] in good yields.[7] We introduce here a formally similar transformation, by which 3-silyl-1-silyloxyallenes are obtained from the reaction of trialkylsilyl ketenes with 1-aryl-2-diazo-2-trialkylsilyl-1-ethanones. In the course of this investigation, we detected a surprisingly simple one-pot preparation of the required α-silyl α-diazo ketones from aryl diazomethyl ketones.

Results and Discussion

Electrophilic silylation of α-diazo ketones with silyl triflates in the presence of a *tert*-amine presents a versatile and practical method to prepare α-silyl α-diazo ketones.[4,8,9] Typically, diethyl ethyl ether is used as the reaction medium, from which most (but not all) of the formed trialkylammonium triflate precipitates as the reaction proceeds. In order to avoid protonation/desilylation of the product by the acidic ammonium salt, Danheiser et al. have used the less polar reaction medium diethyl ether/hexane (1:1), in which the ammonium salt is less soluble, and in fact obtained the silyldiazo ketones in higher yields.[10]

The silylation of diazomethyl ketones **1a**–**c** with trimethylsilyl triflate or triethylsilyl triflate and diisopropylethylamine in ether or diethyl ether/pentane mixtures provided the corresponding α-silyl α-diazo ketones **2a**–**e** (Scheme 1). The synthesis of **2b** and **2d** by this method has been described before,[4,8] but in the present study we prepared only concentrated solutions of **2a**–**e** that were suitable for further transformations (see below). It should be recalled that no α-



2, 3	a	b	c	d	e
Ar	Ph	Ph	C_6H_4-4-OMe	C_6H_4-4-OMe	2-furyl
R	Me	Et	Me	Et	Me

Scheme 1. Synthesis of silyldiazo ketones **2** and silyl ketenes **3**.

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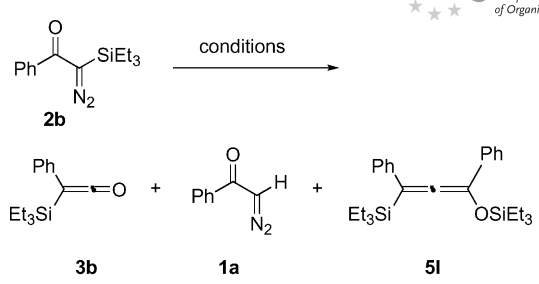
trimethylsilyl-substituted α-diazo ketones have so far been isolated in pure form and that decomposition of **2a** during workup has been reported.[8]

To our surprise, the aryl trialkylsilyl ketenes **3a**–**d** rather than silyldiazo ketones **2** were obtained when the reactions were carried out in dichloromethane or chloroform solution (>95% conversion according to ^{1}H NMR spectroscopy, see for example the spectrum of crude **3c** in the Supporting Information; 60–70% yield after kugelrohr distillation). In these solvents, ammonium triflate **4** is completely soluble, suggesting that it catalyzes the conversion of first-formed diazo ketones **2** into silyl ketenes **3**. In fact, we found that **2c**, prepared in ether solution as described above, is stable in the presence of chloroform for at least 90 min, but gas evolution sets in immediately after addition of ammonium salt **4** and, depending on the amount of **4**, the diazo ketone is either completely converted into silyl ketene **3c** or a mixture of **3c** and allene **5g** (see next paragraph) or, with only 0.1 equiv. of salt **4**, allene **5g** accompanied by small amounts of the original diazomethyl ketone **1b**. A more detailed study was then carried out with purified silyldiazo ketone **2b** (Scheme 2). Again, it was found that ammonium salt **4** was able to convert **2b** into silyl ketene **3b**. However, the reaction time for complete consumption of **2b** was 20 h at 20 °C, even when 1.5 molar equivalents of salt **4** were applied, and the product mixture consisted of ketene **3b**, diazo ketone **1a**, and allene **5l** in a 57:14:29 ratio [^{1}H NMR integration; separation of allene **5l** from ketene **3b** by chromatography or distillation was not possible; NMR spectroscopic data of **5l**: δ(^{1}H) = 0.49–0.55 (m, 12 H), 0.91–0.98 (m, 18 H), 7.18–7.21 (m, 2 H), 7.30–7.37 (m, 6 H), 7.43–7.48 (m, 2 H) ppm]. These results differ partially from those obtained under the conditions for the synthesis of **3b** from **1a** as shown in Scheme 1, where the reaction was over after 2 h at 20 °C and no significant amounts of products other than **3b** could be detected. Thus, there is some evidence that general acid catalysis by the diisopropylethylammonium ion is sufficient to achieve the transformation of silyldiazo ketones **2** into silyl ketenes **3**. However, another catalytic process is also operating and is obviously more relevant.

Taking into account that trialkylsilyl triflates can contain trace amounts of triflic acid (either because of partial hydrolysis or from the production process) that are not eliminated by simple distillation before use, we exposed pure silyldiazo ketone **2b** to a catalytic quantity (1 mol-%) of triflic acid (HOTf) and found that in fact gas evolution started immediately and complete conversion took place within 2 h to yield silyl ketene **3b** and diazo ketone **1b** in a 95:5 ratio. The suspected catalysis by trace amounts of HOTf is also in line with the following observations: (a) Commercial triethylsilyl triflate was typically distilled prior to its use for silylation of the diazo ketones. For a representative sample of Et_3SiOTf, we determined the content of triflic acid by salt formation with diisopropylethylamine (see Supporting Information) as 0.38 wt.%. Then, triethylsilyl triflate was distilled from calcium hydride and directly used for the silylation of ω-diazoacetophenone (**1a**) (CH_2Cl_2, 20 °C, 1.1 equiv. of NEt*i*Pr$_2$); complete conversion of the first-formed silyldiazo ketone **2b** into silyl ketene **3b** was noted only after 14 h (as opposed to 2 h with less pure Et_3SiOTf). (b) Two equivalents of NEt*i*Pr$_2$ were used for the silylation of **1a** with Et_3SiOTf, that is, a 1:1 mixture of Et_3SiOTf and amine was added to a 1:1 mixture of **1a** and amine in dichloromethane. Silyldiazo ketone **2b** was formed as usual, but it remained unchanged in the reaction solution for at least 24 h and no ketene **3b** was formed. Presumably, the presence of a second equivalent of the amine base not only quenches triflic acid effectively, but also deactivates the trialkylammonium ion by formation of a [$R_3N\cdots H^+\cdots NR_3$] complex. *The latter experiment shows that the silyldiazo ketone synthesis can also be carried out successfully in CH_2Cl_2 solution provided that a sufficient excess of the amine base is present.*

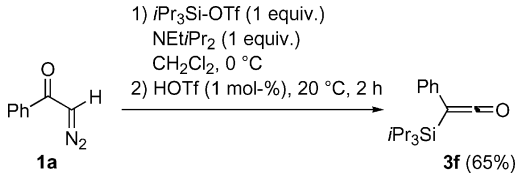


Conditions	Result
*i*Pr$_2$EtN$^+$H $^-$OTf (1.5 equiv.), CH_2Cl_2, 20 °C, 20 h	**3b** : **1a** : **5l**, 57 : 14 : 29
HOTf (1 mol-%), CH_2Cl_2, 20 °C, 2 h	**3b** : **1a**, 95 : 5

Scheme 2. Acid-induced transformation of **2b**.

The formation of silyl ketenes **3** can thus be explained as an acid-induced Wolff-type rearrangement of silyldiazo ketones **2**, which presumably includes O or C protonation of the diazo ketone (vide infra),[11] dediazoniation, and 1,2-aryl migration. Acceleration of the Wolff rearrangement in the presence of protic nucleophiles, such as alcohols and water at neutral pH, has been observed before for other diazo ketones, for example, 1-aryl-2-diazo-2-phenyl-1-ethanones (substituted azibenzils); in contrast, solvolysis of azibenzils by aqueous acids affords only low yields of the ketene-derived diarylacetic acids.[12,13] However, the influence of protons or protic nucleophiles on the decomposition pathways of α-diazo ketones has been a subject of some discussion. On the basis of these investigations and other knowledge of the behavior of α-diazo ketones toward acids,[12] one may assume that silyldiazo ketone **3** is initially O protonated by HOTf to form a β-enoldiazonium ion, which is then transformed into a vinyl cation by loss of N_2; 1,2-aryl shift and proton loss would finally yield silyl ketene **3**. In contrast, C protonation of **3** and counterion-assisted desilylation would explain the formation of small amounts of diazo ketones **1**.

It is obvious from the experiments described above that the direct one-pot synthesis of aryl silyl ketenes **3** from diazo ketones **1** and silyl triflates is somewhat capricious, because the intervening transformation of first-formed silyldiazo ketones **2** into **3** requires acid catalysis. In order to achieve the formation of the silyl ketene in good yield and with short reaction times, we therefore recommend the addition of a catalytic amount (1–4 mol-%) of triflic acid to the reaction mixture when the silylation step is complete. The synthesis of silyl ketene **3f** by this procedure is shown exemplarily in Scheme 3.

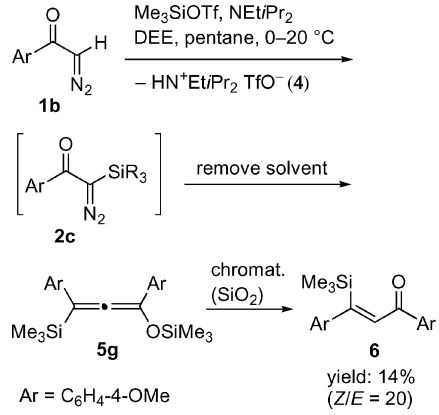


Scheme 3. One-pot synthesis of silyl ketene **3f** by diazo ketone silylation/acid-induced Wolff rearrangement.

The full scope of this transformation for the synthesis of silyl ketenes remains to be explored (e.g., the extension to alkyl silyl ketenes), but it can be stated that the one-pot formation of silyl ketenes **3a**–**d** from diazomethyl ketones **1** and silyl triflates represents a considerable improvement over existing methods. Usually, silyl ketenes are prepared from silyldiazo ketones such as **2** in an additional step by a photochemical[10,14,15] or transition-metal (copper[14] or rhodium[4]) catalyzed Wolff rearrangement.

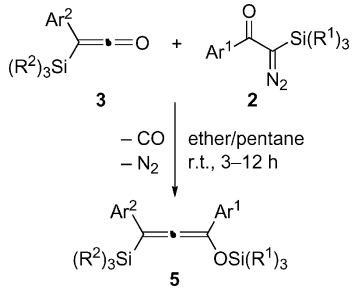
Attempts to isolate silyldiazo ketone **2c** met with another surprise (Scheme 4): diazo ketone **1b** was trimethylsilylated in ether in the presence of NEt*i*Pr$_2$ as usual, the precipitated ammonium salt was filtered off, and the solvent was removed *completely*. A slightly exothermic reaction accompanied by gas evolution started almost immediately to give an oil, from which only β-acylvinylsilane **6** could be isolated in low yield after column chromatography. The assumption that **6** was formed by hydrolysis of allene **5g** during chromatography was later confirmed by treatment of an independently synthesized sample of **5g** with silica gel in chloroform. As the concentrated solution before complete removal of the solvent contained only silyldiazo ketone **2c**, but no silyl ketene or allene, we speculated that in the absence of solvent, **2c** was partly converted into silyl ketene **3c** by the residual (i.e., diethyl ether soluble amounts of) trialkylammonium salt. Allene **5g** would in turn result from a reaction of **2c** with **3c**.

When silyldiazo ketones **2** and silyl ketenes **3** were combined at 0–20 °C, gas evolution began immediately and after reaction times ranging from 3 (**2c** + **3c**) to about 12 h, 1,3-diaryl-3-silyl-1-silyloxyallenes **5** were formed in fairly good yields (Scheme 5 and Table 1). In order to avoid material losses in purification steps, both reactants were used in crude form. The purification of allenes **5** required some experimentation, as they were rather labile towards column chromatography (silica gel or reverse-phase columns) with various eluents. The method of choice turned out to be



Scheme 4. Transformation of silyldiazo ketone **2c** during workup.

chromatography over silica gel with a 20:1 mixture of pentane/diethyl ether. Due to the low water content of this eluent system, hydrolysis of the allene during chromatography could be largely suppressed, and the contamination of the allenes by the corresponding β-acylvinylsilane, if any, was less than 4%. The constitution of allenes **5a** and **5h** was confirmed by XRD analysis (Figures 1 and 2). Spectroscopically, the allenes are characterized by a weak IR absorption at 1901 ± 7 cm^{-1} and the ^{13}C NMR resonance of the central allenic carbon at δ = 204.5–208.0 ppm.



Scheme 5. Synthesis of 3-silyl-1-silyloxyallenes **5**.

Table 1. Synthesis of 3-silyl-1-silyloxyallenes **5** (see Scheme 5).[a]

Allene	Reactants	Ar^1	R^1	Ar^2	R^2	Yield [%]
5a	**2a** + **3a**	Ph	Me	Ph	Me	51
5b	**2c** + **3a**	An	Me	Ph	Me	65
5c	**2e** + **3a**	2-furyl	Me	Ph	Me	84
5d	**2b** + **3a**	Ph	Et	Ph	Me	63
5e	**2d** + **3a**	An	Et	Ph	Me	59
5f	**2a** + **3c**	Ph	Me	An	Me	70
5g	**2c** + **3c**	An	Me	An	Me	71
5h	**2e** + **3c**	2-furyl	Me	An	Me	69
5i	**2b** + **3c**	Ph	Et	An	Me	59
5j	**2d** + **3c**	An	Et	An	Me	83
5k	**2b** + **3d**	Ph	Et	An	Et	69

[a] An = C$_6$H$_4$-4-OCH$_3$.

A mechanistic proposal for the formation of allenes **5** is given in Scheme 6. Previously, we have presented evidence that α-silyl α-diazo ketones **2** are in equilibrium with minute amounts of 1-diazo-2-silyloxyethenes **2′** through a 1,3(C→O) silyl shift.[16] Although the diazo cumulene isomer has not been observed directly so far, it can be

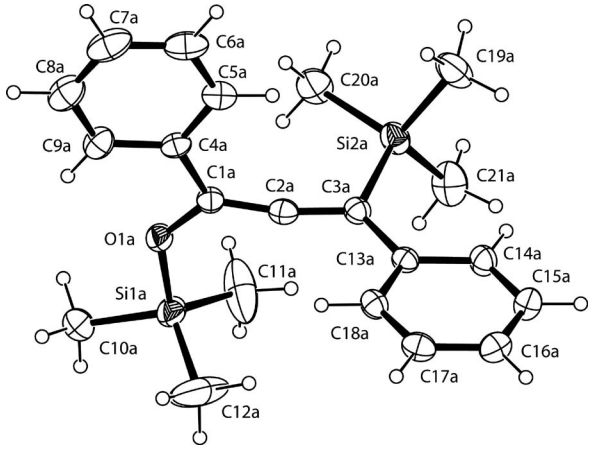


Figure 1. Molecular structure of allene **5a** in the solid state. Thermal displacement ellipsoids are drawn at 30% probability. Selected bond lengths and angles (only one of the two molecules in the asymmetric unit is shown above; data for the second molecule are enclosed in brackets): C1–O1 1.375(3) [1.383(3)], O1–Si1 1.655(2) [1.662(2)], C1–C2 1.320(3) [1.320(3)], C2–C3 1.318(3) [1.318(3)], C3–Si2 1.893(2) [1.899(2)]Å; C1–O1–Si1 129.9(2) [129.0(1)], C1–C2–C3 170.1(2) [172.2(2)], C2–C3–Si2 114.1(2) [114.8(2)]°; torsion angles: C2–C1–C4–C5 9.3(3) [4.9(3)], C2–C3–C13–C18 –5.2(3) [173.9(3)], C2–C1–O1–Si1 10.3(3) [19.1(3)]°.

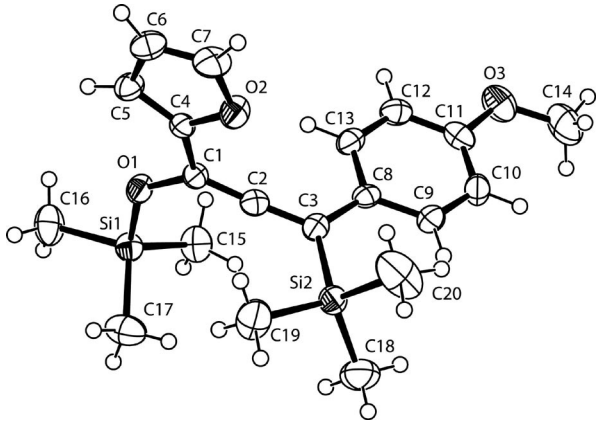
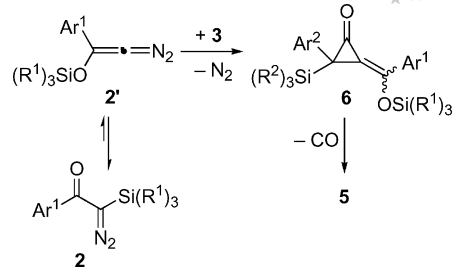


Figure 2. Molecular structure of allene **5h** in the solid state. Thermal displacement ellipsoids are drawn at 50% probability. Selected bond lengths and angles: C1–O1 1.380(3), O1–Si1 1.665(2), C1–C2 1.316(4), C2–C3 1.322(4), C3–Si2 1.898(3) Å; C1–O1–Si1 128.6(2), C1–C2–C3 172.6(3), C2–C3–Si2 115.0(2)°.

trapped selectively by [3+2] cycloaddition with various dipolarophiles, including *N*-phenylmaleimide, norbornene, cyclopropenes, phosphaalkenes, and heterophospholes.[16–18] We assume that diazo cumulenes **2′** add also across the C=C bond of silyl ketenes **3** to form pyrazoline derivatives, which immediately undergo ring contraction to form 2-methylenecyclopropanones **6**, which in turn are decarbonylated to form allenes **5**. The alternative pathway, N_2 extrusion from **2′** and [2+1] cycloaddition of the resulting vinylidene, is disfavored, because these β-arylalkylidene carbenes would undergo rapid 1,2-aryl shift to form silyloxyalkynes.[8]



Scheme 6. Proposed mechanism for the formation of allenes **5**.

Allenes **5** combine the structural and functional moieties of allenylsilanes[19,20] and silyloxyallenes,[21,22] both of which are versatile intermediates in organic synthesis. A few 3-silyl-1-silyloxyallenes have been mentioned in the literature.[20,23] They are easily converted into β-acylvinylsilanes by acidic hydrolysis and by electrophilic C^2-alkylation.

Conclusions

We have made the surprising observation that aryl-substituted α-silyl α-diazo ketones are readily transformed into aryl silyl ketenes in the presence of catalytic amounts of triflic acid. This acid-induced Wolff rearrangement can be combined in a one-pot procedure with the preparation of the silyldiazo ketones from diazomethyl ketones and silyl triflates in the presence of diisopropylethylamine. The trialkylammonium salt, which is formed during the silylation reaction, also seems to catalyze the Wolff rearrangement, but distinctly more slowly than triflic acid. A simple solvent shift from ether (or diethyl ether/pentane), where this salt has low solubility, to dichloromethane, where it is highly soluble, changes the reaction product from the α-silyl α-diazo ketone to the aryl silyl ketene, unless an excess amount of the *tert*-amine base is present.

The prepared ketenes react smoothly with α-silyl α-diazo ketones (or, more likely, with isomeric 2-silyloxy-1-diazoethenes, which coexist in a silatropic equilibrium with the former) to yield 1,3-diaryl-1-silyloxy-3-silylallenes. Further investigations will show whether this reaction type can be extended to silyl ketenes and silyldiazo ketones that bear aliphatic rather than aromatic substituents.

Experimental Section

General Information: All reactions were carried out under an atmosphere of argon by using standard Schlenk techniques. Rigorously dried solvents were used. Kugelrohr distillations were performed with a Büchi GKR 50 apparatus; oven temperatures are reported. Chromatographic purifications were performed on Merck Lobar columns (silica gel Si60, column size B or C). Melting points were determined with a Büchi B-540 apparatus. Infrared spectra (IR) were recorded with a Bruker Vector 22 FTIR spectrometer by using KBr disks for solids and thin films between NaCl plates for liquids. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.62 MHz) spectra were measured with a Bruker DRX 400 spectrometer. All NMR spectra were recorded in $CDCl_3$ at 298 K and are reported in ppm relative to TMS. Mass spectra were obtained with a Bruker micrOTOF-Q

46 instrument by using electron spray ionization (ESI) unless stated otherwise. EI refers to electron ionization.

Starting Materials: Diazo ketones **1a–c** [$ArCOCHN_2$, Ar = Ph (**1a**), 4-methoxyphenyl (**1b**), 2-furyl (**1c**)] were prepared by a published procedure.[24] Trimethylsilyl and triethylsilyl triflate were donated by Chemische Fabrik Karl Bucher GmbH (D-89367 Waldstetten), triisopropylsilyl triflate from Wacker Chemie AG (Munich). All silyl triflates were distilled prior to use and kept under an atmosphere of argon.

General Procedure for the Preparation of Aryl Trialkylsilyl Ketenes 3: A trialkylsilyl triflate (5 mmol) diluted in dichloromethane (5 mL) was added dropwise to a stirred solution of aryl diazomethyl ketone **1** (5 mmol) and diisopropylethylamine (0.88 mL, 5 mmol) in dichloromethane (20 mL) at 0 °C. After completion of the addition, a solution of trifluoromethanesulfonic acid (0.5 M in dichloromethane, 0.1 mL, 0.05 mmol) was added. The solution was stirred at room temperature, and after 2 h, a solution of diisopropylethylamine (0.5 M in dichloromethane, 0.1 mL, 0.05 mmol) was added. The solvent was evaporated at 0.05 mbar/20 °C. Pentane (20 mL) was added, and the precipitated trialkylammonium triflate was filtered off and washed with pentane (10 mL). The volatiles were evaporated at 0.05 mbar/20 °C, and the resulting oil was submitted to kugelrohr distillation.

Ketenes **3b**[4b,8,14] and **3d**[4b] have been synthesized before by photochemical or rhodium-catalyzed decomposition of the corresponding silyldiazo ketone.

2-Phenyl-2-(trimethylsilyl)ethenone (3a): Synthesis by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol). The crude product was purified by kugelrohr distillation (0.06 mbar/80 °C), and **3a** was obtained as a slightly yellow oil (0.57 g, 60%). IR (NaCl, film): $\tilde{\nu}$ = 2959 (m), 2900 (w), 2084 (s, C=C=O), 1598 (m), 1497 (s), 1464 (m), 1411 (s), 1348 (w), 1304 (w), 1253 (s), 1166 (m), 1028 (s), 1001 (m), 948 (m), 925 (m), 843 (s) cm^{-1}. ^1H NMR: δ = 0.34 (s, 9 H), 7.10–7.14 (m, 3 H), 7.28–7.31 (m, 2 H) ppm.^{13}C NMR: δ = –0.3, 24.0, 124.5, 127.8, 129.0, 131.9, 182.6 ppm.

2-Phenyl-2-(triethylsilyl)ethenone (3b). Synthesis by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and triethylsilyl triflate (1.13 mL, 5.0 mmol). The crude product was purified by kugelrohr distillation (0.08 mbar/100 °C), and **3b** was obtained as a slightly yellow oil (0.76 g, 69%). IR (NaCl, film): $\tilde{\nu}$ = 2957 (m), 2912 (m), 2878 (m), 2084 (s, C=C=O), 1597 (m), 1496 (m), 1458 (m), 1415 (w), 1380 (w), 1318 (w), 1262 (m), 1240 (m), 1166 (m), 1072 (m), 1005 (s), 920 (m) cm^{-1}. ^1H NMR: δ = 0.78 (q, ^4J = 7.8 Hz, 6 H), 0.99 (t, ^3J = 7.8 Hz, 9 H), 7.10–7.12 (m, 3 H), 7.24–7.28 (m, 2 H) ppm. ^{13}C NMR: δ = 4.0, 7.1, 20.2, 124.6, 128.0, 128.9, 131.8, 181.8 ppm.

2-(4-Methoxyphenyl)-2-(trimethylsilyl)ethenone (3c). Synthesis by the general procedure from 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol). The crude product was purified by kugelrohr distillation (0.06 mbar/100 °C), and **3c** was obtained as a slightly yellow oil (0.76 g, 69%). IR (NaCl, film): $\tilde{\nu}$ = 2958 (s), 2903 (m), 2836 (m), 2082 (s, C=C=O), 1608 (m), 1578 (w), 1510 (s), 1466 (m), 1442 (m), 1282 (s), 1249 (s), 1180 (s), 1110 (w), 1036 (s), 919 (m), 843 (s) cm^{-1}. ^1H NMR: δ = 0.29 (s, 9 H), 3.79 (s, 3 H), 6.85 (d, ^2J = 8.8 Hz, 2 H), 7.04 (d, ^2J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = –0.4, 22.3, 55.3, 114.6, 122.8, 129.3, 157.2, 182.9 ppm. $C_{12}H_{16}O_2Si$ (220.3): calcd. C 65.4, H 7.3; found C 65.2, H 7.2.

2-(4-Methoxyphenyl)-2-(triethylsilyl)ethenone (3d). Carried out by the general procedure above with 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and triethylsilyl triflate (1.13 mL, 5.0 mmol). The crude product was purified by kugelrohr distillation (0.05 mbar/140 °C), and **3d** was obtained as a slightly yellow oil (0.92 g, 70%). IR (NaCl, film): $\tilde{\nu}$ = 2956 (s), 2911 (m), 2878 (m), 2836 (m), 2085 (s, C=C=O), 1609 (m), 1578 (w), 1510 (s), 1464 (m), 1416 (w), 1281 (m), 1247 (s), 1180 (s), 1109 (w), 1036 (s), 959 (w), 914 (w), 827 (s) cm^{-1}. ^1H NMR: δ = 0.78 (q, ^4J = 7.9 Hz, 6 H), 1.01 (t, ^3J = 7.9 Hz, 9 H), 3.79 (s, 3 H), 6.87 (d, ^2J = 8.7 Hz, 2 H), 7.07 (d, ^2J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 3.9, 7.1, 18.4, 55.1, 114.5, 122.7, 129.5, 157.2, 182.1 ppm.

2-Phenyl-2-(triisopropylsilyl)ethenone (3f). Carried out by the general procedure above with 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and triisopropylsilyl triflate (1.34 mL, 5.0 mmol). The crude product was purified by kugelrohr distillation (0.05 mbar/145 °C), and **3f** was obtained as a slightly yellow oil (0.89 g, 65%). IR (NaCl, film): $\tilde{\nu}$ = 2946 (s), 2891 (m), 2868 (s), 2082 (s, C=C=O), 1596 (m), 1495 (m), 1464 (m), 1385 (w) 1314 (w), 1255 (m), 1169 (m), 1073 (m), 1018 (m), 919 (s), 883 (s) cm^{-1}. ^1H NMR: δ = 1.14 (d, ^3J = 7.3 Hz, 18 H), 1.31 (m, 3 H), 7.13 (t, ^3J = 7.3 Hz, 1 H), 7.19 (d, ^2J = 7.3 Hz, 2 H), 7.26–7.30 (m, 2 H) ppm. ^{13}C NMR: δ = 12.5, 18.5, 19.1, 125.0, 128.9, 129.2, 131.8, 181.9 ppm.

General Procedure for the Preparation of 3-Silyl-1-silyloxyallenes (5): A trialkylsilyl triflate (5.0 mmol) dissolved in dichloromethane (5 mL) was added drop by drop to a stirred solution of aryl diazomethyl ketone **1a–c** (5.0 mmol) and diisopropylethylamine (0.88 mL, 5.0 mmol) in dichloromethane (20 mL) at 0 °C. The resulting solution was stirred at 20 °C for 2 h, and the solvent was evaporated at 0.05 mbar/20 °C. Pentane (20 mL) was added, and the precipitated trialkylammonium triflate was filtered off and washed with pentane (10 mL). After evaporation of the solvent from the combined filtrates at 0.05 mbar/20 °C, silyl ketene **3** was left as a brown oil, which was used without purification.

In a parallel experimental setup, silyldiazo ketone **2** was generated by dropwise addition of a solution of a trialkylsilyl triflate (5.0 mmol) in pentane/diethyl ether (10:1, 22 mL) to a solution of diisopropylethylamine (0.88 mL, 5.0 mmol) and aryl diazomethyl ketone **1** (5.0 mmol) in ethyl ether (18 mL) at 0 °C. The solution was stirred for 2 h at room temperature, the precipitated trialkylammonium triflate was filtered off, and the filtered solution [the presence of **2** was verified by ^{13}C NMR spectroscopy of the reaction solution, e.g., **2c**: δ = 52.9 (CN_2), 191.5 ppm (CO)] was added to crude silyl ketene **3**. The mixture was stirred for 12 h at room temperature, the solvent was evaporated at 0.05 mbar/20 °C, pentane (40 mL) was added to the residue, and the undissolved solid was filtered off and discarded. Pentane was evaporated at 0.05 mbar/20 °C, and the crude product was purified by column chromatography (pentane/diethyl ether, 20:1) to yield 3-silyl-1-silyloxyallenes **5**.

1,3-Diphenyl-3-trimethylsilyl-1-trimethylsilyloxy-1,2-propadiene (5a): Preparation by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3a**, and 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyldiazo ketone **2a**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5a** was obtained as a slightly yellow oil, which solidified immediately to give colorless crystals (0.89 g, 51%). M.p. 71–72 °C. IR (NaCl, film): $\tilde{\nu}$ = 2956 (m), 2897 (w), 1898 (m, C=C=C), 1593 (m), 1577 (w), 1490 (m), 1448 (m), 1407 (w), 1346 (s), 1263 (s), 1248 (s), 1192 (m), 1176 (m), 1072 (m), 1061 (m), 1024 (m), 999 (w), 870 (s), 839 (s) cm^{-1}. ^1H NMR: δ = 0.19 (s, 9 H), 0.31 (s, 9 H), 7.19–7.25 (m, 2 H), 7.29–7.40 (m, 6 H), 7.47–7.49 (m, 2 H) ppm. ^{13}C NMR: δ = –0.1, 0.2, 117.7, 124.0, 126.0, 126.7, 127.0,

127.9, 128.2, 128.5, 135.6, 137.3, 204.5 ppm. $C_{21}H_{28}OSi_2$ (352.6): calcd. C 71.53, H 8.00; found C 71.34, H 8.02.

1-(4-Methoxyphenyl)-3-phenyl-3-trimethylsilyl-1-trimethylsilyloxy-1,2-propadiene (5b): Preparation by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3a**, and 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyldiazo ketone **2c**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5b** was obtained as a yellow oil (1.25 g, 65%). IR (NaCl, film): $\tilde{\nu}$ = 2957 (s), 2900 (m), 2836 (w), 1903 (w, C=C=C), 1723 (w), 1607 (s), 1579 (w), 1509 (s), 1489 (m), 1443 (m), 1417 (w), 1350 (s), 1250 (s), 1170 (s), 1109 (m), 1077 (w), 1060 (m), 1033 (s), 1008 (w), 876 (s), 839 (s) cm^{-1}. ^1H NMR: δ = 0.17 (s, 9 H), 0.30 (s, 9 H), 3.81 (s, 3 H), 6.87–6.89 (m, 2 H), 7.20–7.24 (m, 1 H), 7.29–7.40 (m, 6 H) ppm. ^{13}C NMR: δ = –0.1, 0.2, 55.3, 113.8, 117.7, 125.3, 126.0, 126.9, 127.8, 128.1, 128.5, 137.5, 158.7, 207.7 ppm. MS (ESI): m/z = 383.2 $[M - H]^+$.

1-(2-Furyl)-3-phenyl-3-trimethylsilyl-1-trimethylsilyloxy-1,2-propadiene (5c): Preparation by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3a**, and 2-diazo-1-(2-furyl)ethanone (**1c**) (0.68 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyldiazo ketone **2e**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5c** was obtained as a yellow oil (1.43 g, 84%). IR (NaCl, film): $\tilde{\nu}$ = 2960 (m), 2899 (w), 1908 (w, C=C=C), 1596 (w), 1520 (w), 1489 (m), 1447 (m), 1408 (w), 1382 (w), 1334 (s), 1252 (s), 1220 (m), 1193 (s), 1158 (m), 1125 (w), 1089 (m), 1062 (m), 1006 (s), 928 (m), 902 (w), 842 (s) cm^{-1}. ^1H NMR: δ = 0.17 (s, 9 H), 0.29 (s, 9 H), 6.35–6.37 (m, 1 H), 6.42–6.43 (m, 1 H), 6.85–6.87 (m, 2 H), 7.21–7.25 (m, 1 H), 7.30–7.39 (m, 5 H) ppm. ^{13}C NMR: δ = –0.3, 0.1, 106.4, 111.3, 118.9, 120.0, 127.0, 128.0, 128.4, 137.5, 141.7, 149.5, 205.9 ppm.

1,3-Diphenyl-1-triethylsilyloxy-3-trimethylsilyl-1,2-propadiene (5d): Preparation by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3a**, and 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5 mmol) and triethylsilyl triflate (1.13 mL, 5 mmol) for silyldiazo ketone **2b**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5d** was obtained as a slightly yellow oil (1.25 g, 63%). IR (NaCl, film): $\tilde{\nu}$ = 2957 (s), 2912 (m), 2877 (m), 1900 (w, C=C=C), 1596 (m), 1518 (w), 1491 (m), 1449 (m), 1413 (w), 1379 (w), 1345 (m), 1260 (s), 1191 (m), 1119 (w), 1074 (m), 1061 (m), 1005 (m), 975 (w), 944 (w), 916 (w) 873 (w), 837 (s) cm^{-1}. ^1H NMR: δ = 0.30 (s, 9 H), 0.67 (q, 6 H), 0.94 (t, 9 H) 7.19–7.25 (m, 2 H), 7.30–7.38 (m, 6 H), 7.47–7.51 (m, 2 H) ppm. ^{13}C NMR: δ = –0.2, 4.7, 6.7, 117.6, 124.0, 125.9, 126.7, 126.9, 127.8, 128.2, 128.4, 135.7, 137.4, 207.5 ppm. MS (ESI): m/z = 395.2 $[M - H]^+$.

1-(4-Methoxyphenyl)-3-phenyl-1-triethylsilyloxy-3-trimethylsilyl-1,2-propadiene (5e): Preparation by the general procedure from 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3a**, and 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and triethylsilyl triflate (1.13 mL, 5.0 mmol) for silyldiazo ketone **2d**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5e** was obtained as a yellow oil (1.24 g, 59%). IR (NaCl, film): $\tilde{\nu}$ = 2956 (s), 2911 (m), 2877 (m), 2836 (w), 1903 (w, C=C=C), 1654 (w), 1605 (s), 1578 (m), 1509 (s), 1489 (m), 1461 (m), 1416 (m), 1349 (s), 1250 (s), 1170 (s), 1108 (m), 1107 (m), 1077 (m), 1060 (m), 1034 (s), 1005 (m), 974 (w), 916 (w), 836 (s) cm^{-1}. ^1H NMR: δ = 0.29 (s, 9 H), 0.64 (q, ^4J = 7.8 Hz, 6 H), 0.93 (t, ^3J = 7.9 Hz, 9 H), 3.81 (s, 3 H), 6.87–6.89 (m, 2 H), 7.20–7.24 (m, 1 H), 7.29–7.32 (m, 2 H), 7.35–7.37 (m, 2 H), 7.40–7.43 (m, 2 H) ppm. ^{13}C NMR: δ = –0.16, 4.7, 6.7, 55.3, 113.8, 117.7, 125.3, 126.0, 126.8, 127.8, 128.0, 128.4, 137.7, 158.7, 208.0 ppm. MS (ESI): m/z = 425.2 $[M - H]^+$.

3-(4-Methoxyphenyl)-1-phenyl-3-trimethylsilyl-1-trimethylsilyloxy-1,2-propadiene (5f): Preparation by the general procedure from 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3c**, and 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyldiazo ketone **2a**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5f** was obtained as white crystals (1.35 g, 70%). M.p. 78–79 °C. IR (NaCl, film): $\tilde{\nu}$ = 2958 (s), 2900 (m), 2836 (w), 1899 (w, C=C=C), 1604 (s), 1577 (w), 1507 (s), 1492 (m), 1449 (m), 1414 (w), 1345 (m), 1250 (s), 1193 (m), 1172 (s), 1110 (w), 1062 (m), 1037 (m), 1024 (m), 910 (m), 874 (s), 841 (s) cm^{-1}. ^1H NMR: δ = 0.19 (s, 9 H), 0.30 (s, 1 H), 3.81 (s, 3 H), 6.85–6.87 (m, 2 H), 7.12–7.22 (m, 1 H), 7.30–7.34 (m, 4 H), 7.45–7.47 (m, 2 H) ppm. ^{13}C NMR: δ = –0.1, 0.2, 55.2, 113.9, 116.9, 124.1, 125.9, 126.6, 128.2, 129.0, 129.4, 135.8, 158.7, 205.8 ppm. $C_{22}H_{30}O_2Si_2$ (382.6): calcd. C 69.06, H 7.90; found C 68.93, H 7.72.

1,3-Bis(4-methoxyphenyl)-3-trimethylsilyl-1-trimethylsilyloxy-1,2-propadiene (5g): Preparation by the general procedure from 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3c**, and 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyldiazo ketone **2c**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5g** was obtained as a colorless oil (1.48 g, 71%). IR (NaCl, film): $\tilde{\nu}$ = 2957 (s), 2901 (w), 2836 (w), 1901 (w, C=C=C), 1651 (w), 1605 (s), 1578 (m), 1507 (s), 1464 (m), 1442 (m), 1418 (w), 1349 (m), 1287 (m), 1249 (s), 1192 (m), 1170 (s), 1109 (m), 1062 (m), 1035 (s), 1008 (w), 911 (m), 876 (s), 840 (s) cm^{-1}. ^1H NMR: δ = 0.17 (s, 9 H), 0.29 (s, 9 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 6.84–6.88 (m, 4 H), 7.31–7.39 (m, 4 H) ppm. ^{13}C NMR: δ = 0.0, 0.2, 55.3 (2 C), 113.8, 113.9, 116.9, 125.3, 128.1, 129.0, 129.8, 158.7, 158.7, 206.3 ppm. MS (ESI, addition of $AgNO_3$): m/z = 519.1 $[M + Ag]^+$.

1-(2-Furyl)-3-(4-methoxyphenyl)-3-trimethylsilyl-1-trimethylsilyloxy-1,2-propadiene (5h): Preparation by the general procedure from 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3c**, and 2-diazo-1-(2-furyl)ethanone (**1c**) (0.68 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyldiazo ketone **2e**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5h** was obtained as a colorless oil (1.28 g, 69%). IR (NaCl, film): $\tilde{\nu}$ = 2959 (m), 2900 (w), 2837 (w), 1905 (w, C=C=C), 1605 (m), 1577 (w), 1508 (s), 1463 (w), 1442 (w), 1413 (w), 1382 (w), 1332 (m), 1250 (s), 1220 (m), 1195 (s), 1173 (s), 1158 (m), 1110 (w), 1086 (m), 1063 (m), 1037 (m), 1006 (m), 924 (m), 907 (m), 842 (s) cm^{-1}. ^1H NMR: δ = 0.17 (s, 9 H), 0.29 (s, 9 H), 3.81 (s, 3 H), 6.34–6.35 (m, 1 H), 6.41–6.43 (m, 1 H), 6.85–6.87 (m, 2 H), 7.32–7.34 (m, 3 H) ppm. ^{13}C NMR: δ = –0.2, 0.1, 55.2, 106.2, 111.3, 113.8, 118.1, 119.9, 129.2, 129.6, 141.7, 149.7, 158.8, 204.5 ppm.

3-(4-Methoxyphenyl)-1-phenyl-1-triethylsilyloxy-3-trimethylsilyl-1,2-propadiene (5i): Preparation by the general procedure with 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3c**, and 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and triethylsilyl

triflate (1.13 mL, 5.0 mmol) for silyldiazo ketone **2b**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5i** was obtained as a yellow oil (1.26 g, 59%). IR (NaCl, film): $\tilde{\nu}$ = 2956 (s), 2911 (m), 2877 (m), 2836 (w), 1898 (w, C=C=C), 1604 (s), 1577 (w), 1508 (s), 1492 (m) 1462 (m), 1449 (m), 1414 (s), 1379 (s), 1344 (m), 1250 (s), 1193 (m), 1172 (s), 1110 (w), 1062 (m), 1037 (s), 1024 (m), 975 (w), 910 (m), 838 (s) cm^{-1}. ^1H NMR: δ = 0.29 (s, 9 H), 0.65 (q, 6 H), 0.94 (t, 9 H), 3.84 (s, 3 H), 6.84–6.86 (m, 2 H), 7.18–7.21 (m, 1 H), 7.30–7.34 (m, 4 H), 7.47–7.49 (m, 2 H) ppm. ^{13}C NMR: δ = –0.1, 4.7, 6.7, 55.2, 113.9, 116.8, 124.1, 125.8, 126.6, 128.2, 129.0, 129.6, 135.9, 158.7, 206.0 ppm.

1,3-Bis(4-methoxyphenyl)-1-triethylsilyloxy-3-trimethylsilyl-1,2-propadiene (5j): Preparation by the general procedure from 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and trimethylsilyl triflate (0.91 mL, 5.0 mmol) for silyl ketene **3c**, and 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and triethylsilyl triflate (1.13 mL, 5.0 mmol) for silyldiazo ketone **2d**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5j** was obtained as an orange oil (1.90 g, 83%). ^1H NMR: δ = 0.29 (s, 9 H), 0.65 (q, 6 H), 0.95 (t, 9 H), 3.810 (s, 3 H), 3.813 (s, 3 H), 6.84–6.89 (m, 4 H), 7.30–7.42 (m, 4 H) ppm. ^{13}C NMR: δ = –0.1, 4.7, 6.7, 55.2, 55.3, 113.7, 113.8, 116.8, 125.3, 125.8, 128.2, 128.9, 129.8, 158.6, 206.4 ppm.

3-(4-Methoxyphenyl)-1-phenyl-1-triethylsilyloxy-3-triethylsilyl-1,2-propadiene (5k): Preparation by the general procedure from 2-diazo-1-(4-methoxyphenyl)ethanone (**1b**) (0.88 g, 5.0 mmol) and triethylsilyl triflate (1.13 mL, 5.0 mmol) for silyl ketene **3d**, and 2-diazo-1-phenylethanone (**1a**) (0.73 g, 5.0 mmol) and triethylsilyl triflate (1.13 mL, 5.0 mmol) for silyldiazo ketone **2b**. The crude product was purified by column chromatography (pentane/diethyl ether, 20:1), and **5k** was obtained as a colorless oil (1.61 g, 69%). IR (NaCl, film): $\tilde{\nu}$ = 2955 (s), 2911 (s), 2876 (s), 2835 (m), 1895 (w, C=C=C), 1604 (s), 1577 (w), 1507 (s) 1492 (m), 1460 (m), 1414 (m), 1379 (w), 1343 (m), 1286 (m), 1248 (s), 1192 (m), 1171 (s), 1109 (w), 1057 (m), 1037 (m), 1006 (s), 974 (m), 897 (w), 830 (s) cm^{-1}. ^1H NMR: δ = 0.63–0.67 (m, 6 H), 0.78–0.82 (m, 6 H), 0.91–0.99 (m, 18 H), 3.81 (s, 3 H), 6.83–6.85 (m, 2 H), 7.12–7.21 (m, 1 H), 7.29–7.33 (m, 4 H), 7.49–7.51 (m, 4 H) ppm. ^{13}C NMR: δ = 4.3, 4.8, 6.7, 7.6, 55.2, 113.8, 114.6, 124.1, 125.3, 126.5, 128.1, 128.8, 130.1, 136.1, 158.7, 207.4 ppm.

1,3-Bis(4-methoxyphenyl)-3-trimethylsilylprop-2-en-1-one (6): A solution of ω-diazoacetophenone (1.76 g, 10.0 mmol) and diisopropylethylamine (1.74 mL, 10.0 mmol) in diethyl ether (60 mL) was cooled to 0 °C, and a solution of trimethylsilyl triflate (1.81 mL, 10.0 mmol) in diethyl ether (50 mL) was added drop by drop. After the addition was complete, the mixture was brought to room temperature and stirred for 2 h. The precipitated diisopropylethylammonium triflate was filtered off, and the solvent was completely removed at 15 mbar. A yellow oil was left, which started to undergo a slightly exothermic reaction with vigorous gas evolution within a minute (***CAUTION!***). After 30 min, the viscous oil was extracted with pentane (3 × 50 mL). The extracts were combined and concentrated, and the residue was subjected to column chromatography over silica gel (90 g; $CHCl_3$/pentane, 4:1). The first fraction (the following ones were discarded because of the low amount of product) furnished a yellow oil (0.48 g) that was dissolved in a small volume of pentane. After several days at –18 °C, yellow crystals of **6** were obtained (0.23 g, 14%). M.p. 88–89 °C. ^1H NMR: δ = 0.21 (s, 9 H), 3.82 (s, 3 H), 3.88 (s, 3 H), 6.92–6.95 (m, 2 H), 6.98 (s, 1 H), 7.07–7.10 (m, 1 H), 7.15–7.19 (m, 2 H), 7.32–7.37 (m, 2 H), 7.43–7.45 (m, 1 H), 7.86–7.81 (m, 2 H) ppm. ^{13}C NMR: δ = 0.3, 55.2, 55.5, 113.4, 113.8, 127.8, 130.9, 131.04, 137.46, 138.36, 158.57, 163.34, 164.03, 190.19 ppm. MS (EI, 70 eV): *m/z* (%) = 340 (21) $[M]^+$, 325 (100), 310 (18), 309 (11), 290 (17), 267 (10), 260 (12), 248 (15), 195 (9), 192 (9), 135 (16), 107 (10). $C_{20}H_{24}O_3Si$ (340.5): calcd. C 70.5, H 7.10; found C 70.5, H 7.09.

Crystal-Structure Determination for 5a and 5h: Crystals were obtained from pentane solution. The data collection was performed with an image-plate diffractometer (Stoe IPDS) by using monochromated Mo-K_α radiation (λ = 0.71073 Å). Both structures were solved by direct methods and refined with a full-matrix least-squares method by using F^2 values. Hydrogen atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. Software for structure solution and refinement: SHELX-97;[25] molecule plots: ORTEP-3.[26] Further details are provided in Table 2.

Table 2. Crystallographic data and details of data collection and structure refinement for **5a** and **5h**.

	5a	**5h**
Empirical formula	$C_{21}H_{28}OSi_2$	$C_{20}H_{28}O_3Si_2$
Formula weight	352.6	372.6
Temperature [K]	193(2)	193(2)
Crystal size [mm]	0.23 × 0.15 × 0.04	0.38 × 0.23 × 0.12
Crystal system	monoclinic	monoclinic
Space group	*P* $2_1/n$	*P* $2_1/n$
a [Å]	16.825(2)	8.901(1)
b [Å]	14.488(1)	20.008(2)
c [Å]	18.702(2)	12.292(2)
α [°]	90	90
β [°]	110.27(1)	97.31(2)
γ [°]	90	90
V [Å^3]	4276.5(9)	2171.4(5)
Z	8	4
Density [g cm^{-3}]	1.095	1.140
μ(Mo-K_α) [mm^{-1}]	0.931	0.178
F (000)	1088	800
θ range [°]	2.32–25.03	2.52–25.03
Reflections collected	30440	15580
Independent reflections (R_{int})	7256 (0.0750)	3663 (0.1205)
Completeness to θ_{max} [%]	96.1	95.6
Data/restraints/parameters[a]	7256/0/445	3663/0/233
Goodness-of-fit on F^2	0.825	0.869
Final *R* indices [$I > 2\sigma(I)$]: R_1, wR_2 [b]	0.0389, 0.0824	0.0524, 0.1075
R indices (all data): R_1, wR_2 [b]	0.0825, 0.0947	0.0975, 0.1178
Largest diff. peak and hole [e Å^{-3}]	0.24, –0.23	0.31, –0.30

[a] Refinement based on F^2 values. [b] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o||$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

CCDC-661871 (for **5a**) and -687385 (for **5h**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR spectra for compounds **2c**, **3a**–**d**,**f**, and **5a**–**k**; procedure to determine the acid content in triethylsilyl triflate.

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